247. Carbon Participation in the Solvolysis of Tertiary Norbornyl Derivatives

Norbornanes, Part 15[1])

6-Substituted 2-Methylnorbornyl 2-*exo*- and 2-*endo*-2,4-Dinitrophenyl Ethers

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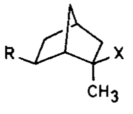
Summary

The solvolysis rates and products of the tertiary 2-methyl-2-*exo*- and -2-*endo*-norbornyl 2,4-dinitrophenyl ethers **1** and **2**, ($X = 2,4\text{-}(NO_2)_2C_6H_3O$) have been determined. The different sensitivities of the rates of these ethers to the inductive effect of substituents at C(6) indicate that graded bridging of C(2) by C(6) occurs in the ionization of the *exo*-ethers **1**, not, however, in the ionization of the *endo*-ethers **2**. In both cases hydrolysis leads to 2-methyl-2-*exo*-norbornanols only. Consequently, substitution takes place with retention at C(2) in the *exo*-series **1** and with inversion at C(2) in the *endo*-series **2**. It is concluded that stereoelectronic and polar effects, rather than steric bulk effects, determine the high *exo*/*endo* rate ratios of the parent norbornyl derivatives **1a** and **2a**.

Introduction. – Solvolyses of tertiary 2-norbornyl derivatives, such as the 2-methyl-2-*exo*- and -2-*endo*-norbornyl *p*-nitrobenzoates **1a** and **2a** ($X = p\text{-}NO_2C_6H_4COO$), respectively, have played an important role in the debate over the fine structure of the 2-norbornyl cation[2]). Like their secondary analogs **3a** and **4a**, the tertiaries display high *exo*/*endo* rate ratios of the order of 10^2 to 10^3, a finding which led *Brown* to propose his steric hypothesis, namely, that the rates of *exo*-norbornyl derivatives are normal, whereas the rates of their *endo*-epimers are retarded due to sterically hindered departure of the nucleofuge X in **2** and **4** [1].



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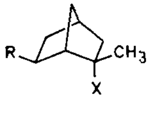

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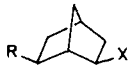

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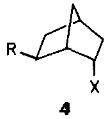

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R = a) H
b) CH_3
c) i-C_3H_7
d) CH_2Br
e) $COOCH_3$
f) CH_3COO
g) COONa
h) CH_2OH

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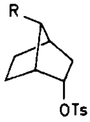
[1]) The IUPAC name for (Norbornane) is 8,9,10-trinorbornane.

[2]) For a comprehensive review see [1].

Meanwhile, it has been shown that the rates of the *secondary* 6-substituted 2-*exo*-norbornyl *p*-toluenesulfonates (tosylates) **3** (X = OTs) are far more sensitive to the inductive *(I)* effect of the substituents than the rates of the 2-*endo*-epimers **4** [2] and of the 7-*anti*-substituted 2-*endo*-tosylates **5** [3]. This finding implied that inductivity [4] is especially high in the secondary 2-*exo*-6-*exo*-series **3** and led to the conclusion that through-space induction involves graded participation, or bridging, of C(6) in the ionization step. Bridging is strong in the incipient ion pair **7** when R is an electron donor and weaker or absent when R is an electron acceptor relative to the cationic center[3]).



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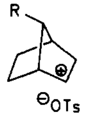

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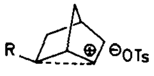

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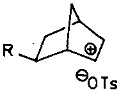

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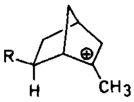
The much lower inductivity of the *endo*-tosylates **4** (X = OTs) was attributed to repulsion of the electrons around C(6) by the anion in the incipient ion pair **8**. The even lower inductivity of the tosylates **5** (X = OTs) was considered to be due to the large increase in strain which accompanies the bridging of C(2) by the dorsal C(7) during ionization to **6**, for it involves the division of a five-membered ring into a strained four and a three membered ring, whereas the six-membered ring in **7** is divided into a less strained five- and a three-membered ring [5].



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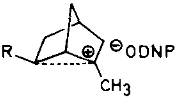

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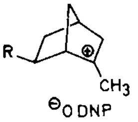

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Table 1. *Yield of Products* (in %) *from the Reaction of* 6-exo-*Substituted 2-Methylnorbornyl* 2-exo-(**1**) *and* (in brackets) 2-endo-*Dinitrophenyl Ethers* (**2**) *in 70%* (v/v) *Dioxane*

	R	**12**	**13**	**14**
a	H	24 (37)	30 (14)	46 (49)
b	CH_3	45 (46)	22 (12)	33 (42)
c	i-C_3H_7	46 (42)	21 (13)	33 (45)
d	CH_2Br	20 (31)	32 (3)	48 (66)
e	$COOCH_3$	12 (23)	35 (4)	53 (73)
f	CH_3COO	9 (16)	35 (4)	56 (80)
g	COONa	51 (58)[a])	17 (3)	32 (30)
h	CH_2OH	36 (52)	26 (4)	38 (44)

[a]) Also 9% of the 2-*endo*-alcohol **15**.

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[3]) For a review of this work see [4] [5].

Table 2. *First-Order Rate Constants*ᵃ) *for* 10^{-3}M 6-exo-*Substituted* 2-endo-*Methyl-2*-exo-*norbornyl 2,4-Dinitrophenyl Ethers* **1a–h** *in* 80% (v/v) *EtOH*, $3 \cdot 10^{-3}$M *in* Et_3N

Compound	R	T [°C]	k [s^{-1}]	$H^{\neq}$ [kcal/mol]	$S^{\neq}$ [cal/mol degree]
1a	H	49.90	$1.68 \cdot 10^{-4}$	23.59	−2.95
		59.97	$5.31 \cdot 10^{-4}$		
		69.97	$1.53 \cdot 10^{-3}$		
		100.00	$2.70 \cdot 10^{-2}$ b)		
1b	CH_3	49.97	$2.10 \cdot 10^{-4}$	25.27	2.69
		60.02	$7.23 \cdot 10^{-4}$		
		69.89	$2.19 \cdot 10^{-3}$		
		100.00	$4.77 \cdot 10^{-2}$ b)		
1c	i-C_3H_7	49.88	$3.29 \cdot 10^{-4}$	24.48	1.14
		60.32	$1.11 \cdot 10^{-3}$		
		70.28	$3.37 \cdot 10^{-3}$		
		100.00	$6.35 \cdot 10^{-2}$ b)		
1d	CH_2Br	79.97	$2.64 \cdot 10^{-4}$	27.13	1.58
		89.98	$8.00 \cdot 10^{-4}$		
		99.68	$2.15 \cdot 10^{-3}$		
		100.00	$2.23 \cdot 10^{-3}$ b)		
1e	$COOCH_3$	100.00	$3.98 \cdot 10^{-4}$ b)	26.70	−2.98
		109.75	$1.04 \cdot 10^{-3}$		
		119.75	$2.46 \cdot 10^{-3}$		
		129.80	$6.28 \cdot 10^{-3}$		
1f	CH_3COO	99.85	$5.75 \cdot 10^{-5}$	29.54	0.81
		100.00	$5.86 \cdot 10^{-5}$ b)		
		120.21	$4.81 \cdot 10^{-4}$		
		129.64	$1.18 \cdot 10^{-3}$		
1g	COONa c)	50.02	$3.57 \cdot 10^{-4}$	27.47	10.52
		60.00	$1.33 \cdot 10^{-3}$		
		69.85	$4.49 \cdot 10^{-3}$		
		100.00	$1.27 \cdot 10^{-1}$ b)		
1h	CH_2OH	60.02	$3.75 \cdot 10^{-4}$	25.92	3.25
		69.98	$1.20 \cdot 10^{-3}$		
		80.00	$3.64 \cdot 10^{-3}$		
		100.00	$2.78 \cdot 10^{-2}$ b)		

a) Measured conductometrically.
b) Extrapolated.
c) With 3 equiv. of NaOH.

In view of the importance of 1,3-bridging in the ionization of the secondary *exo*-tosylates **3** there is no apparent reason why it should be absent in the ionization of tertiary *exo*-norbornyl derivatives, as claimed by *Brown* [1], *Schleyer et al.* [6]⁴) and *Takeuchi et al.* [7]. Undoubtedly, increased charge dispersal in the tertiary carbocation **9** will reduce the interaction between C(2) and a dipolar substituent at C(6). Nevertheless, the positive charge centered at C(2) should still attract the electrons surrounding C(6) and, hence, induce bridging. In fact, partial bridging, as illustrated in the cation in

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4) See also [1], pp. 145 and 149.

Table 3. *First-Order Rate Constants*[a] *for* 10^{-3}M 6-exo-*Substituted* 2-exo-*Methyl*-2-endo-*norbornyl 2,4-Dinitrophenyl Ethers* **2a–h** *in 80%* (v/v) *EtOH*, $3 \cdot 10^{-3}$M *in* Et_3N

Compound	R	T [°C]	k [s^{-1}]	H^* [kcal/mol]	S^* [cal/mol degree]
2a	H	89.70	$5.73 \cdot 10^{-5}$	26.08	−6.49
		99.70	$1.51 \cdot 10^{-4}$		
		100.00	$1.58 \cdot 10^{-4}$ [b]		
		109.70	$4.00 \cdot 10^{-4}$		
2b	CH_3	99.55	$1.67 \cdot 10^{-4}$	28.12	−0.83
		100.00	$1.75 \cdot 10^{-4}$ [b]		
		109.59	$4.61 \cdot 10^{-4}$		
		119.58	$1.22 \cdot 10^{-3}$		
2c	i-C_3H_7	99.96	$1.27 \cdot 10^{-4}$	27.99	−1.80
		100.00	$1.28 \cdot 10^{-4}$ [b]		
		109.98	$3.56 \cdot 10^{-4}$		
		120.00	$9.16 \cdot 10^{-4}$		
2d	CH_2Br	100.00	$2.14 \cdot 10^{-5}$ [b]	28.45	−4.12
		119.91	$1.59 \cdot 10^{-4}$		
		129.63	$3.78 \cdot 10^{-4}$		
		140.12	$9.92 \cdot 10^{-4}$		
2e	$COOCH_3$	100.00	$7.70 \cdot 10^{-6}$ [b]	31.05	0.83
		119.85	$6.74 \cdot 10^{-5}$		
		130.04	$1.87 \cdot 10^{-4}$		
		140.22	$5.03 \cdot 10^{-4}$		
2f	CH_3COO	100.00	$4.20 \cdot 10^{-6}$ [b]	30.24	−2.55
		129.65	$9.12 \cdot 10^{-5}$		
		139.91	$2.39 \cdot 10^{-4}$		
2g	COONa [c]	89.57	$1.10 \cdot 10^{-4}$	23.92	−11.07
		99.65	$2.87 \cdot 10^{-4}$		
		100.00	$2.89 \cdot 10^{-4}$ [b]		
		109.66	$6.62 \cdot 10^{-4}$		
2h	CH_2OH	100.00	$1.08 \cdot 10^{-4}$ [b]	27.41	−3.68
		109.94	$2.87 \cdot 10^{-4}$		
		120.00	$7.48 \cdot 10^{-4}$		
		129.54	$1.74 \cdot 10^{-3}$		

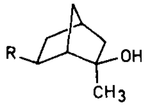
[a] Measured conductometrically.

[b] Extrapolated.

[c] With 3 equiv. of NaOH.

10, was postulated long ago by *Paasivirta* [8] to explain the rapid formation of the *exo*-formate **1a** (X = HCOO) from the tertiary *exo*-alcohol **1a** (X = OH) with HCOOH, *i.e.* with retention of configuration. Furthermore, *Olah et al.* [9] ascribed the remarkable deshielding of H_{exo}–C(6) in the ^{1}H–NMR spectrum of the free tertiary cation **9** (R = H) by 2.19 ppm, as compared to H_{endo}–C(6), to selective withdrawal of electron density from the C(6)–H_{exo} bond, *i.e.* to partial bridging. The same conclusion based on kinetic and thermodynamic data was drawn by *Sorensen et al.* [10].

The case for bridging in tertiary norbornyl cations could be strengthened if it were to be shown that inductivity is substancially higher in solvolyses of 2-*exo*-derivatives of 6-substituted 2-methylnorbornanes **1** than in the *endo*-epimers **2**. Unfortunately, the corresponding tosylates **1** and **2** (X = OTs) are not isolable. However, *Brown & Ikegami* have prepared and measured the rates of the *p*-nitrobenzoates **1a** and **2a** (X = $p-NO_2C_6H_4COO$) [11]. They also reported an *exo/endo* rate ratio of 885 for these compounds in 80% acetone at 25°. But these esters proved to be unreactive or prone to ester hydrolysis in 80% EtOH when -*I*-substituents were introduced at C(6). Consequently, the 2-*exo*- and 2-*endo*-(2,4-dinitrophenyl) ethers **1** and **2**, **a–h**, (X = 2,4-$(NO_2)_2C_6H_3O$) were employed in the present study. Their preparation and their hydrolysis products in 70% dioxane (*Table 1*) are described in the accompanying paper [12]. This article reports their rate constants in 80% EtOH, measured by the conductometric method [2] (*Tables 2* and *3*), and the inductivities thus derived[5]).



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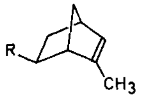

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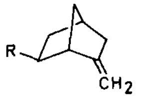

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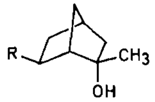

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Results and Discussion. – As *Table 1* shows, hydrolysis of the tertiary *exo*-(**1**) and *endo*-2,4-dinitrophenyl ethers **2a–h** (X = 2,4-$(NO_2)_2C_6H_3O$) yielded the corresponding *exo*-alcohols **12a–h**, only. The small amounts of the *endo*-alcohol **15g** obtained from the *endo*-ether **2g** are obviously formed by nucleophilic attack of excess NaOH at C(1′) of the dinitrophenyl group. The *exo*-ethers **1** thus react exclusively with retention of configuration at C(2), the *endo*-ethers **2** with inversion at C(2). This result alone is evidence for C(6)–C(2) bridging in the cation of the incipient ion pairs **10** from **1** and for its absence in the cations of the *endo* ion pairs **11** from **2**. The main products, however, were the *endo*- and *exo*-cyclic olefins **13** and **14** (*Table 1*). It is noteworthy that no rearranged products were detected.

The relative rates of the *exo*- and *endo*-ethers **1** and **2**, **a–h**, cover a range of 2167 and 69, respectively. Accordingly, the *exo/endo* rate ratios drop from 491 for R = i-C_3H_7 to 14 for R = CH_3COO (*Table 4*). They would undoubtedly decrease further if stronger electron-attracting substituents were introduced, regardless of their bulk. Therefore, polar rather than steric effects control *exo/endo*-ratios in these tertiary ethers.

This is also illustrated by the plots of log *k* for the ethers **1** and **2**, **a–f**, against the respective inductive substituents constants σ_I^q [14] (*Fig. 1*). In accordance with the *Hammett*-type equation $\log k/k_0 = \varrho_I \cdot \sigma_I^q$ linear correlations are obtained, which proves the dominance of *I*-effects. The points for R = COONa and CH_2OH were not included in the regression because these substituents are electrofugal groups [15], *i.e.* electron donors, which have regularly displayed exalted *I*-effects in S_N1 processes [2] [16][6])[7]).

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[5]) Some of the results were reported in preliminary communications [13].

[6]) The *exo*-ethers **1g** and **1h** are accelerated by factors of 17 and 4.3, the *endo*-ethers **2g** and **2h** by factors of 5.5 and 2.2, respectively, based on the regression line in *Fig. 1*.

[7]) The appearance of exalted *I*-effects of electrofugal groups in processes involving carbocations is due to the fact that pK_a-values of 4-substituted quinuclidinium salts were employed to derive σ_I^q-values, *i.e.* ammonium salts which possess full electron shells.

Table 4. *Relative Rates and* exo/endo *Rate Ratios for the Ethers* **1** *and* **2** (**a–h**) *at 100°*

R		*k*(rel)		
		exo-ethers **1**	*endo*-ethers **2**	*exo*/*endo*
a	H	461	38	171
b	CH_3	801	42	272
c	i-C_3H_7	1082	31	491
d	CH_2Br	38	5.1	105
e	$COOCH_3$	7	1.8	52
f	CH_3COO	1	1	14
g	COONa	2167	69	439
h	CH_2OH	474	26	257

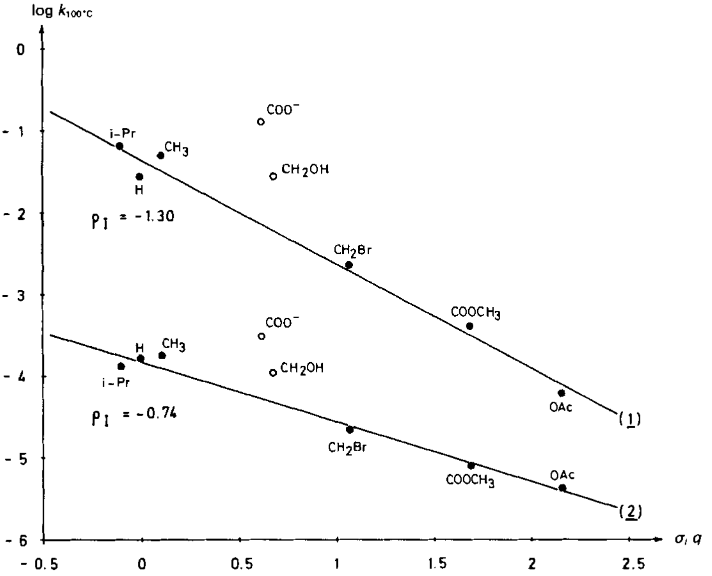
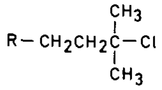


Fig. 1. *Plots of log* k *for 6-substituted 2-methyl-2-*exo- (**1**) *and -2-*endo- (**2**) *norbornyl 2,4-dinitrophenyl ethers in 80%* (v/v) *EtOH* vs. *the inductive substituent constants* σ_I^q. Electrofugal substituents (open circles) not included in the regression.

The slopes of the converging regression lines in Figure 1 correspond to reaction constants ϱ_I of -1.30 and -0.74, respectively. As expected, the inductivities of the tertiary *exo*- and *endo*-ethers differ markedly, though not as strongly as those of the secondary *exo*- and *endo*-tosylates **3** ($\varrho_I = -2.0$) and **4** ($\varrho_I = -0.86$) [2a]. Greater charge dispersal thus lowers the tendency for tertiary cations to be bridged. It is noteworthy that ϱ_I for the *endo*-series **2** (-0.74) is close to that for the acyclic tertiary chlorides **16** (-0.71) which ionize without appreciable carbon participation [17]. It can, therefore, be concluded that in the *endo*-series **2** bridging of C(2) by C(6) is greatly reduced due to repulsion by the departing anion, as was also the case in the secondary *endo*-series **4**.

Since bridging of C(2) by C(7) is at a minimum in the latter series [3] it should be negligible in the case of the series **2**.



$$R-CH_2CH_2\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-Cl$$

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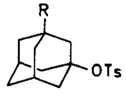

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When the log *k* values for the *exo*- and *endo*-ethers **1** and **2**, **a–h**, in 80% EtOH are plotted against the log *k* values for the corresponding 3-substituted adamantyl tosylates **17** [16b], satisfactory linear correlations are obtained *(Fig. 2)*. The respective slopes of 1.1 and 0.67 indicate that in the *exo*-series **1** inductivity is almost equal to that of **17**, whereas in the *endo*-series **2** inductivity is considerably smaller. However, since the rates of the tertiary tosylates **17** are controlled by the *I*-effects of the substituents and not by steric bulk effects [16], the same must apply to the series **1** and **2**.

Because of the widely different reactivities of tertiary and secondary norbornyl derivatives[8]) it is practically impossible to compare their inductivities with the same nucleofugal group. However, ϱ_I-values do not vary much with the leaving group [16b]; also changes appear to depend primarily on ground state crowding, *i.e.* on a steric bulk effect [16b]. Since the steric requirements of aryl sulfonates and 2,4-dinitrophenyl ethers

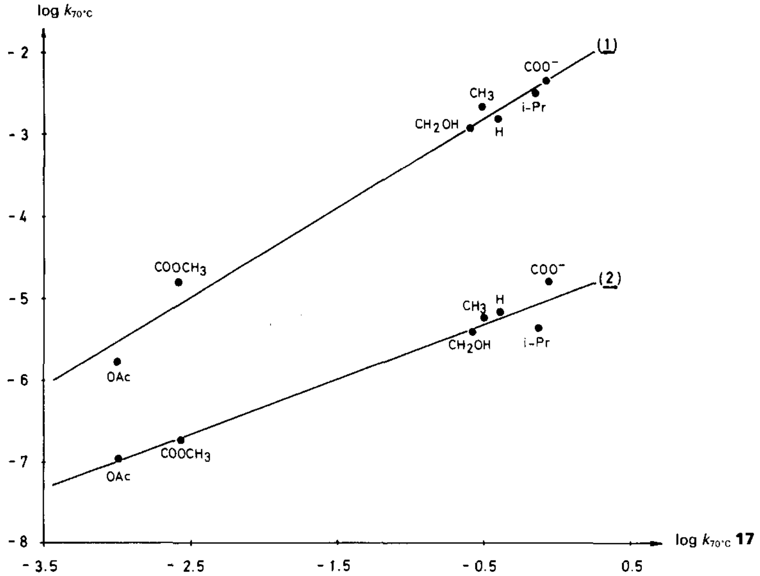

Fig. 2. *Plots of log* k *for 6-substituted 2-methyl-2-*exo-(**1**) *and -2-*endo-(**2**) *norbornyl 2,4-dinitrophenyl ethers* vs. log k *for 3-substituted adamantyl tosylates* (**17**)

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[8]) In solvolytic fragmentation of α-aminoketoximes the tosylates were shown to be *ca.* 10^6 times as reactive as 2,4-dinitrophenyl ethers [18].

are similar, it can be concluded that the ϱ_I values for the hypothetical tosylates **1** and **2** (X = OTs) do not differ substancially from those found for the ethers **1** and **2** (X = 2,4-$(NO_2)_2C_6H_3O$). A comparison of the tertiary and secondary compounds **1–4** is, therefore, justified.

Conclusion. – The rates and the products of the 6-substituted tertiary 2-*exo*- and 2-*endo*-norbornyl 2,4-dinitrophenyl ethers **1** and **2** indicate that differential bridging in the transition state, rather than a steric bulk effect, is responsible for high *exo/endo* rate ratios.

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